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## (54) POLYIMIDE PRECURSOR SOLUTION AND POLYAMIDE COATING FILM OBTAINABLE THEREFROM

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a polyimide precursor solution which has a low viscosity even when it contains the solute of a polyimide precursor in a solvent at a high solids content ratio and does not cause cissing of a coating liquid against a substrate upon coating and is difficult to be affected by the state of the substrate surface, and a polyimide coating film having no pinhole at a thickness of ≤10 μm and excellent surface smoothness.
SOLUTION: This polyimide precursor solution comprises a salt composed of 3,4'-oxydianiline and 3,3',4,4'-biphenyltetracarboxylic acid and/or its derivative and 4,4'-oxydiphthalic acid and/or its derivative which is dissolved as the solute in an organic solvent with a molar ratio of the tetracarboxylic acid and/or its derivative of 0:100 to 90:10, and 0.001-5 pts. mass, based on 100 pts. mass salt as the solute, surface active agent containing a siloxane unit. The polyamide coating film has a thickness of ≤10 μm which can be obtained by coating this solution on a substrate and imidating the coated film.

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CLAIMS

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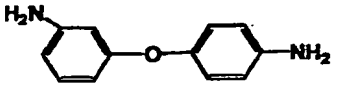
[Claim(s)]
[Claim 1] 3 and 4'-oxy-dianyline which are shown in the following type (1), 3 and 3' which are shown in the following formula (2), and the salt which consists of 4 shown in - biphenyl tetracarboxylic acid and/or its derivative, and the following type (3), a 4 and 4'4'-oxy-JIFUTARU acid, and/or its derivative are dissolving into an organic solvent as solutes. Mole ratios with 4 shown in - biphenyl tetracarboxylic acid, and/or its derivative and formula (3), a 3 and 3', 4, and 4'4'-oxy-JIFUTARU acid, and/or its derivative are 0:100-90:10. [ which are shown in said formula (2) ] And the polyimide precursor solution characterized by carrying out 0.001-5 mass section content of the surfactant including the siloxane unit shown in the following type (4) to the salt 100 mass section as a solute.
[Formula 1]



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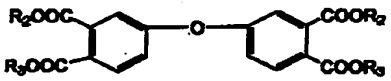

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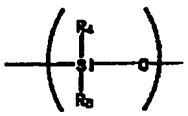

(4)

(The inside R and R1 of a formula, R2, and R3 are independently chosen from a hydrogen atom and the alkyl group of carbon numbers 1-5, respectively, and R4 and R5 are independently chosen from a hydrogen atom, the alkyl group of carbon numbers 1-5, an alkoxy group, and a phenyl group, respectively.)
[Claim 2] The polyimide precursor solution according to claim 1 characterized by for the concentration of the salt as a solute being 30 to 80 mass %, and solution viscosity being 10poise or less.
[Claim 3] The polyimide coat characterized by the thickness obtained by carrying out coating of the polyimide precursor solution according to claim 1 or 2 on a substrate, and heating-imide-izing being 10 micrometers or less.

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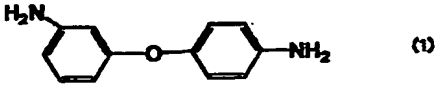
## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the polyimide precursor solution containing a surfactant including a siloxane unit, and the polyimide coat which reaches and is obtained.
[0002]
[Description of the Prior Art] Conventionally, the polyimide which was excellent in electric insulation or high thermal resistance as the surface protective coats and interlayer insulation films of various electronic parts, such as a semiconductor device, was used widely. Moreover, although the laminating of an anode plate, an organic electroluminescence layer, and the cathode is carried out one by one and they consist of organic electroluminescence displays (organic electroluminescence display) which make a current pass and emit light to the fluorescent substance formed on the glass substrate or the transparent organic film on a substrate, the thin film of polyimide is used as an insulator layer between said anode plates and said organic electroluminescence layers. Polyimide is used as an insulating protective coat further again also on the metal substrate applied to a solar battery. Since these organic electroluminescence displays and a solar battery are laminating phase structures, it is required of the polyimide coat applied as the thickness of 10 micrometers or less that there are no outstanding surface smooth nature and outstanding pinhole.
[0003] By the way, the spray coating method which makes the bar coating-machine method and coating liquid the shape of a fog, and is sprayed on a substrate as an approach of making a polyimide coat forming, or the spin coat method which carries out coating according to a centrifugal force is known. The spin coat method is used especially suitable for thickness making a thin film 10 micrometers or less form. Although viscosity of the coating liquid used for a spin coat method needed to be made into 10poise or less at 20 degrees C, when the viscosity of coating liquid was low, at the time of coating, HAJIKI to the substrate of the liquid which carried out coating occurred, and there was a problem that minute irregularity was made in a coat on a pinhole or a front face.
[0004] The polyimide coating liquid used on the other hand in case a polyimide coat is formed was a polyimide precursor solution which uses dimethylacetamide and N-methyl pyrrolidone as a solvent and makes polyamic acid a solute, and was difficult to originate in the polymerization degree of polyamic acid being high and the solubility to a solvent being small, and to make the solid content ratio in a solution high in this case. If put in another way, the polyimide precursor solution which used conventional polyamic acid as the polyimide precursor had the essential problem that viscosity was high, although solid content concentration was low, and polyamic acid was high polymerization therefore. When carrying out coating of the polyimide precursor solution which used this polyamic acid as the polyimide precursor with a spin coat method, that solid content concentration needed to be reduced extremely. Therefore, the polyimide thin film obtained from conventional polyimide coating liquid had the problem of being scarce in surface smooth nature, in order that the marks of few [ a coating substrate front face ] cracks and foreign matters, and irregularity might remain in a coat front face, since the solid content concentration of coating liquid was low.

[0005] As mentioned above, when thickness tended to obtain a polyimide coat 10 micrometers or less conventionally, there was a problem that polyimide coating liquid is using what has low viscosity, HAJIKI on a substrate will occur if coating of the coating liquid with low viscosity is carried out on a substrate, and a pinhole occurred on the polyimide coat obtained as a result. Moreover, when the solid content concentration of polyimide coating liquid was low, it was influenced by the condition on the front face of a substrate, and was easy, and there was also a problem that the surface smooth nature of the polyimide coat obtained was low.
[0006]
[Problem(s) to be Solved by the Invention] An example is taken by such situation. The 1st technical problem of this invention The polyimide precursor solution which it is hypoviscosity and HAJIKI to the substrate of the liquid which carried out coating at the time of coating does not occur even if the polyimide precursor which is a solute contains by the high solid content ratio in a solvent, and is not influenced by the condition on the front face of a substrate is offered, Moreover, thickness does not have a pinhole at 10 micrometers or less, and the 2nd technical problem has it in offering the polyimide coat which is excellent in surface smooth nature with sufficient productivity.
[0007]
[Means for Solving the Problem] The result of having inquired wholeheartedly in order that this invention persons might solve the above-mentioned technical problem, The polyimide precursor solution containing the surfactant which the salt which consists of specific diamine, a carboxylic acid, and/or its derivative is dissolving in the organic solvent as a solute, and has a specific structural unit Even if it has the high solid content ratio, it is hypoviscosity, and there is no HAJIKI to the substrate of the liquid which carried out coating, and it found out that it could not be easily influenced by the condition on front faces of a substrate, such as the crack or irregularity on the front face of a substrate, and a foreign matter. And a pinhole did not occur, but the polyimide coat obtained from this solution found out having surface smooth nature, and reached this invention.
[0008] Namely, 3 and 4'-oxy-dianyline which show the summary of this invention in the following formula (1) the 1st, 3 and 3' which are shown in the following formula (2), and the salt which consists of 4 shown in - biphenyl tetracarboxylic acid and/or its derivative, and the following type (3), a 4 and 4'4'-oxy-JIFUTARU acid, and/or its derivative are dissolving into an organic solvent as solutes. Mole ratios with 4 shown in - biphenyl tetracarboxylic acid, and/or its derivative and formula (3), a 3 and 3', 4, and 4'4'-oxy-JIFUTARU acid, and/or its derivative are 0:100-90:10. [ which are shown in said formula (2) ] And it is the polyimide precursor solution characterized by carrying out 0.001-5 mass section content of the surfactant including the siloxane unit shown in the following type (4) to the salt 100 mass section as a solute.
[0009]
[Formula 2]



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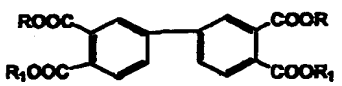

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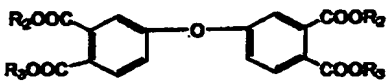

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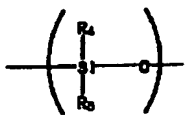
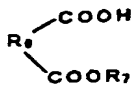


(4)

[0010] (The inside R and R1 of a formula, R2, and R3 are independently chosen from a hydrogen atom and the alkyl group of carbon numbers 1-5, respectively, and R4 and R5 are independently chosen from a hydrogen atom, the alkyl group of carbon numbers 1-5, an alkoxy group, and a phenyl group, respectively.)
It is the polyimide precursor solution characterized by for the concentration of the salt as a solute being 30 to 80 mass %, and solution viscosity being 10poise or less in said polyimide precursor solution the 2nd. It is the polyimide coat characterized by the thickness obtained [ 3rd ] by carrying out coating of the above and the polyimide precursor solution on a substrate, and heating-imide-izing being 10 micrometers or less.
[0011]
[Embodiment of the Invention] This invention is explained to a detail below. First, the vocabulary used by this invention is explained.
(1) Say the organic polymer in which more than 80 mol % of the repeat unit of a polyimide polymer chain has imide structure. And this organic polymer shows thermal resistance.
(2) Say polyimide precursor heating or the organic compound which carries out a ring closure according to a chemical operation, and serves as polyimide. Here, a ring closure means that an imide ring structure is formed.
(3) The polyimide precursor solution polyimide precursor is dissolving in the solvent. A solvent means a liquefied compound at 25 degrees C here.
[0012] (4) Measure the rotation viscosity in 20 degrees C using viscosity TOKIMEC [, INC. ], INC. make and a DVL-BII mold digital viscometer (Brookfield viscometer).
(5) It is the numeric value which expressed with the percentage the mass rate of the polyimide precursor occupied in a solute concentration solution.
(6) Using the DEJIMA [ by thickness Mitutoyo Corp. ] tic micrometer of a polyimide coat, measure the thickness of a polyimide coat by ten places, and ask as the average.
(7) The longitudinal-plane-of-symmetry average of roughness height (SRa) of the polyimide coat front face formed on the substrate front face or the substrate was measured using the surface smooth nature three-dimension surface roughness measuring device (the Kosaka lab company make ET-30K, sensing-pin measurement), and smooth nature of a substrate front face or a polyimide coat front face was evaluated from the numeric value.
[0013] Furthermore, this invention is explained. 3 and 4'-oxy-dianyline which show the salt which is a solute in a formula (1) in the polyimide precursor solution of this invention, In 3 and 3' which are shown in a formula (2), [type (2) which consists of 4 shown in - biphenyl tetracarboxylic acid and/or its derivative, and a formula (3), a 4 and 4'4'-oxy-JIFUTARU acid, and/or its derivative, and a formula (3) R, R1, R2, and R3 respectively -- independent -- ****** from a hydrogen atom and the alkyl group of carbon numbers 1-5. ] . And as for the mole ratio with 4 shown in - biphenyl tetracarboxylic acid, and/or its derivative and formula (3), a 3 and 3', 4, and 4'4'-oxy-JIFUTARU acid, and/or its derivative, 0:100-90:10 are desirable. [ which are shown in a formula (2) ] When the mole ratio of the 4 and 4'-oxy-JIFUTARU acid shown in a formula (3) and/or its derivative is less than ten, the adhesion force to the substrate of the polyimide coat obtained may decline, and a coat may exfoliate from a substrate.
[0014] In the polyimide precursor solution of this invention, you may transpose to the dicarboxylic acid anhydride which shows a part of tetracarboxylic acid shown in a formula (2) and (3), and/or its derivative in the carboxylic acid shown in a general formula (5), or a general formula (6). At this time, as for the mole ratio of the sum of the tetracarboxylic acid shown in a formula (2) and (3), and/or the number of mols of that derivative, and the dicarboxylic acid anhydride shown in the carboxylic acid shown in a general formula (5), or a general formula (6), 100:0-100:20 are desirable, and 100:0-100:11 are still more desirable. If the mole ratio of the dicarboxylic acid anhydride shown in the carboxylic acid shown in the general formula (5) to the sum 100 of the tetracarboxylic acid shown in a formula (2) and (3) and/or its number of derivative mols or a general formula (6) exceeds 20, only a polyimide coat with low reinforcement may be obtained.
[0015]
[Formula 3]



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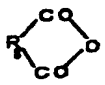
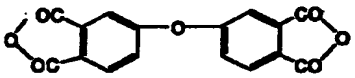


(6)

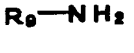
[0016] As for the inside R6 of [type, divalent aromatic series residue including at least one membered-rings [ six ] directly connected with the carbon atom with which two carbonyl groups adjoined is expressed, R7 expresses a hydrogen atom or the alkyl group of carbon numbers 1-5, and R8 expresses divalent aromatic series residue including at least one membered-rings [ six ] directly connected with the carbon atom with which two carbonyl groups adjoined. ]
[0017] Furthermore, you may transpose to 4 shown in - biphenyl tetracarboxylic dianhydride and/or formula (8), and 3 and 3', 4, and 4'4'-oxy-JIFUTARU acid 2 anhydride. [ which show a part of tetracarboxylic acid shown in a formula (2) and (3), and/or its derivative in a formula (7) ] As for the mole ratio of the sum of the tetracarboxylic acid shown in a formula (2) and (3), and/or the number of mols of that derivative, and the sum of the number of mols of tetracarboxylic dianhydride shown in a formula (7) and (8), at this time, 100:0-70:30 are desirable. The viscosity of a polyimide precursor solution can be finely tuned by adjusting this mole ratio. If the sum of the number of mols of tetracarboxylic dianhydride shown in a formula (7) and (8) exceeds 30-mol %, the hypoviscosity polyimide precursor solution which is the description of this invention may be unable to be obtained.
[0018]
[Formula 4]

(7)



(8)

[0019] Furthermore, you may transpose to the amine of one functionality which shows a part of 3 and 4'-oxy-dianyline shown in a formula (1) in a general formula (9). In this case, as for the mole ratio of the amine shown in the general formula (9) to the 3 and 4'-oxy-dianyline shown in a formula (1), it is desirable that it is 100:0-100:20, and 100:0-100:11 are still more desirable. If the amine shown in a general formula (9) exceeds 20-mol %, only a polyimide coat with low reinforcement may be obtained. The inside R9 of [type expresses aromatic series residue including at least one membered-rings [ six ]. ]
[0020]
[Formula 5]



(9)

[0021] Moreover, the inside R4 of the surfactant [type which includes the siloxane unit shown in a formula (4) to the salt 100 mass section which is a solute in the polyimide precursor solution of this invention, and R5 are independently chosen from a hydrogen atom, the alkyl group of carbon numbers 1-5, an alkoxy group, and a phenyl group, respectively. ] 0.001 - 5 mass section -- 0.001 - 1 mass section is made to contain preferably When coating of the polyimide precursor solution is carried out to the content of a surfactant being under the 0.001 mass section at a substrate, HAJIKI to the substrate of the liquid which carried out coating may occur. On the other hand, if a surfactant exceeds 5 mass sections, film production nature falls, a crack and a crack occur, and a uniform coat may not be obtained.
[0022] HAJIKI of the liquid which carried out coating to metal substrates, such as organic material substrates, such as a glass substrate, a ceramic substrate, and polyimide, aluminum, copper, gold, silver, and nickel, stops generating the polyimide precursor solution of this invention

by making a surfactant including a siloxane unit contain at an above rate.
[0023] As a surface active agent including the siloxane unit which can be used by this invention, a leveling agent with easy acquisition, a defoaming agent, a foam stabilizer, etc. are mentioned, and the dimethylpolysiloxane which specifically carried out polyether conversion, the methyl alkyl polysiloxane which carried out polyether conversion, the dimethylpolysiloxane which carried out polyester conversion, the methyl alkyl polysiloxane which carried out polyester conversion, the methyopolysiloxane which carried out aralkyl conversion are mentioned.
[0024] As for the concentration of the polyimide precursor in the polyimide precursor solution of this invention, it is desirable that it is 30 to 80 mass %. It is more desirable that it is 40 to 80 mass %. If concentration is lower than 30 mass %, the blemish on the front face of a substrate which carries out coating, a foreign matter, and irregularity may remain as irregularity on the front face of a coat. On the other hand, since it may become difficult to dissolve a polyimide precursor stably according to the class of solvent to select if concentration is higher than 80 mass %, it is not desirable.
[0025] The solution viscosity of the polyimide precursor solution of this invention has desirable 10poise or less. 10poise or more of the fluidity of coating liquid is not enough, and when thickness produces a coat 10 micrometers or less especially in a spin coat method, since the coat of uniform thickness may be [ that thickness nonuniformity tends to happen ] unproducible, it is not desirable.
[0026] 3 which shows the polyimide precursor solution in this invention in a formula (1), and 4 -- 4 shown in - biphenyl tetracarboxylic acid and/or its derivative, and a formula (3), a '3 shown in - oxy-dianyline and formula (2), 3', 4, and 4'4'-oxy-JIFUTARU acid, and/or its derivative can be manufactured by carrying out sequential addition to an organic solvent. What kind of sequence is sufficient as the sequence to add.
[0027] Although it will not be limited especially if the organic solvent used by this invention dissolves the polyimide precursor and surfactant which are a solute For example, N-methyl pyrrolidone, dimethyl formamide, dimethylacetamide, Dimethyl sulfoxide, hexa methyl phosphoryl TORIAMIDO, a sulfolane, The polar solvent and Cellosolve which contain N, S, and P atom in molecules, such as N and N'-dimethyl imidazolidinone and N-methyl caprolactam, Acetic-acid Cellosolve, such as Cellosolve, such as phenyl Cellosolve, ethyl-acetate Cellosolve, and butyl-acetate Cellosolve Carbitols, such as methyl carbitol and ethyl carbitol, ethyl-acetate carbitol, Acetic-acid carbitols, such as butyl-acetate carbitol, dimethyl carbitol (jig lime), Ketones, such as alcohols, such as carbitol diethers, such as diethyl carbitol, a cyclohexanol, and benzyl alcohol, a cyclohexanone, and an isophorone, gamma-butyrolactone, etc. are mentioned.
[0028] The usual approach is adopted as the coating approach for obtaining a polyimide coat from the polyimide precursor solution of this invention, for example, approaches, such as a spin coat method, a spray coating method, and the bar coating-machine method, are mentioned, and when thickness produces the thin film excellent in surface smooth nature 10 micrometers or less, a spin coat method is used suitably. Also in the coating approaches other than a spin coat method, if the polyimide precursor solution of this invention is used, as compared with the case where a polyimide coat is manufactured using the conventional polyimide precursor solution, the polyimide coat excellent in surface smooth nature can be obtained.
[0029] After it carries out coating of the polyimide precursor solution on a substrate or a base material, and it dries and it removes a solvent, a polyimide coat obtains the paint film of a polyimide precursor, imide-izes this and obtains a polyimide coat. Furthermore, it exfoliates from a base material, or a polyimide film will be obtained, if it exfoliates from a base material and the paint film of a polyimide precursor is imide-ized. In this invention, a polyimide film enters under the category of a polyimide coat. 150 degrees C or more, preferably, imide-ization is 250 degrees C or more, more than for 10 minutes, is preferably heated more than for 30 minutes, and is performed 200 degrees C or more.
[0030] furthermore -- the polyimide precursor solution of this invention -- the need -- responding -- for example, a pigment, conductive carbon black and a bulking agent like metal particles, an attrition agent, a dielectric, lubricant, etc. -- others -- a well-known additive can be added in the range which does not spoil the effectiveness of this invention. Moreover, solvents,

such as other polymers, the ether of for example, water-insoluble nature, alcohols, ketones, ester, halogenated hydrocarbon, and hydrocarbons, can be added in the range which does not spoil the effectiveness of this invention.

[0031] Since it has the polyimide coat obtained from the polyimide precursor solution of this invention, and the surface smooth nature which was [ that there is nothing ] excellent especially in the polyimide coat with a thickness of 10 micrometers or less with regards to the crack and foreign matter on the front face of a substrate, or irregularity, excluding a pinhole, it is suitably used as a surface protective coat, an interlayer insulation film, etc., for example, it is used for a solar-battery substrate, an EL element substrate, the component for a heat-resistant insulation, a capacitor, etc. Moreover, it can use for manufacture of these products also in the polyimide precursor solution of this invention.

[0032]

[Example] Hereafter, this invention is explained to a detail using an example.

270.0g (ODPA) (0.87 mols) of 4 and 4'-oxy-JIFUTARU acids was dissolved in N-methyl pyrrolidone 500g as example 1 solvent, and, subsequently methanol 83.56g (2.61 mols) and triethylamine 4.18g were added. With the internal temperature of 80 degrees C, the esterification reaction of this solution was carried out by the warm water bath in bottom 2 hours of stirring, and the solution containing 4 and 4'-oxy-JIFUTARU acid dimethyl ester was obtained. After cooling this reaction solution to 50 degrees C, 3 and 4'-oxy-dianyline 174.29g (0.87 mols) was added, the stirring dissolution was carried out for 2 hours, and the uniform polyimide precursor solution was obtained. Furthermore, 2.5g which is 0.5 mass % was added to the solid content of a polyimide precursor solution which was able to obtain surface-active-agent BYK-302 (made in big KEMI Japan, dimethylpolysiloxane which carried out polyether conversion) including a siloxane unit, the stirring dissolution was carried out until the system became homogeneity at 25 degrees C, and the polyimide precursor solution (black) was obtained (solid content concentration 50 mass %). When the viscosity of this solution was measured, it was 1.8poise at 20 degrees C. Furthermore, coating of this solution was carried out on the 8 inch-silicon wafer substrate in engine-speed 4,000rpm and 30 seconds using the spin coater (the Mikasa, Inc make, 1 H-DX). Under the present circumstances, HAJIKI to the substrate of the liquid which carried out coating was not generated. Then, after drying the liquid which carried out coating at 80 degrees C under nitrogen-gas-atmosphere mind for 5 hours, heating imide-ization was performed at 300 degrees C under nitrogen-gas-atmosphere mind for 5 hours, and the polyimide coat with a thickness of 2 micrometers was obtained. The pinhole in this polyimide coat was not observed.

[0033] Furthermore, the spin coat of this solution was similarly carried out to the aluminum substrate (diameter of 100mm) whose longitudinal-plane-of-symmetry average of roughness height (SRa) is 50nm, heat imide-ization was performed, and the polyimide coat was obtained. The pinhole was not observed, but further, the thickness of the obtained polyimide coat is 2 micrometers, and it was [ SRa is 0.5nm and ] very excellent in surface smooth nature.

[0034] The polyimide coat was made to form by the same approach as an example 1 except [ all ] having used the glass substrate which the longitudinal-plane-of-symmetry average of roughness height (SRa) is 40nm, and is the diameter of 100mm as an example 2 coating substrate. At the time of coating, HAJIKI to the substrate of the liquid which carried out coating was not generated. The thickness of the obtained polyimide coat was 2 micrometers, it was not observed, but SRa was 0.7nm, and the pinhole was what is excellent in surface smooth nature.

[0035] Except [ all ] setting example 3 surface active agent to BYK-333 (made in big KEMI Japan, dimethylpolysiloxane which carried out polyether conversion) including a siloxane unit, it reacted on the same preparation and same conditions as an example 1, and the polyimide precursor solution (black) was obtained. When the viscosity of this solution was measured, they were 20 degrees C and 1.8poise. The polyimide coat was made to form furthermore on the aluminum substrate (diameter of 100mm) whose SRa is 50nm on the same approach and same conditions as an example 1 about this solution. At the time of coating, HAJIKI to the substrate of the liquid which carried out coating was not generated. The thickness of the obtained polyimide coat was 2 micrometers, the pinhole within a coat side was not observed and SRa was 0.4nm.

[0036] Except [ all ] setting example 4 surfactant to SH193 (the Toray Industries Dow Corning make, conversion silicone oil) including a siloxane unit, it reacted on the same preparation and same conditions as an example 1, and the polyimide precursor solution (black) of this invention was obtained. The viscosity of this solution was 1.8poise at 20 degrees C. The polyimide coat was made to form furthermore on the aluminum substrate (diameter of 100mm) whose SRa is 50nm on the same approach and same conditions as an example 1 about this solution. At the time of coating, HAJIKI to the substrate of the liquid which carried out coating was not generated. The thickness of the obtained polyimide coat was 2 micrometers, the pinhole within a coat side was not observed and SRa was 0.5nm.

[0037] 3, 3', and 70.9g (BPDA) (0.24 mols) of - biphenyl tetracarboxylic acid and 174.5g (ODPA) (0.56 mols) of 4 and 4 '4, 4'-oxy-JIFUTARU acids were dissolved in N-methyl pyrrolidone 500g as example 5 solvent, and, subsequently methanol 77.13g (0.24 mols) and triethylamine 3.86g were added (the mole ratio of BPDA and ODPA is 7:3). With the internal temperature of 80 degrees C, the esterification reaction of this solution was carried out at the warm water bath in bottom 2 hours of stirring, and 3, 3', and the solution containing 4 and 4 '- biphenyl tetracarboxylic acid dimethyl ester, 4, 4'-oxy-JIFUTARU acid dimethyl ester (the mole ratio of 3, 3', 4, and 4 '- biphenyl tetracarboxylic acid dimethyl ester, 4, 4'-oxy-JIFUTARU acid dimethyl ester is 7:3) were obtained. After cooling this reaction solution to 50 degrees C, 3 and 4'-oxy-dianyline 160.9g (0.80 mols) was added, the stirring dissolution was carried out for 2 hours, and the uniform polyimide precursor solution was obtained. Furthermore, the polyimide precursor solution (black) was obtained by carrying out the stirring dissolution until it added 2.3g which is 0.5 mass % to the solid content of a polyimide precursor solution which was able to obtain surface-active-agent BYK-302 (made in big KEMI Japan, dimethylpolysiloxane which carried out polyether conversion) including a siloxane unit and the system became homogeneity at 25 degrees C (solid content concentration 48 mass %). When the viscosity of this solution was measured, it was 1.7poise at 20 degrees C. Furthermore on the same conditions as an example 1, coating of this solution was carried out on the 8 inch-silicon wafer substrate using the spin coater. Under the present circumstances, HAJIKI to the substrate of the liquid which carried out coating was not generated. Then, after drying a coating object at 80 degrees C under nitrogen-gas-atmosphere mind for 5 hours, heating imide-ization was performed at 300 degrees C under nitrogen-gas-atmosphere mind for 5 hours, and the polyimide coat with a thickness of 2 micrometers was obtained. The pinhole was not observed by this polyimide coat. Furthermore, the spin coat of this solution was similarly carried out to the aluminum substrate (diameter of 100mm) whose SRa is 50nm, heat imide-ization was performed, and the polyimide coat was obtained. The pinhole was not observed, but further, the thickness of the obtained polyimide coat is 2 micrometers, and it was [ SRa is 0.5nm and ] very excellent in surface smooth nature.

[0038] 3, 3', and 104.8g (BPDA) (0.36 mols) of - biphenyl tetracarboxylic acid and 110.5g (ODPA) (0.36 mols) of 4 and 4 '4, 4'-oxy-JIFUTARU acids were dissolved in N-methyl pyrrolidone 500g as example 6 solvent, and, subsequently methanol 68.37g (2.13 mols) and triethylamine 3.42g were added (the mole ratio of BPDA and ODPA is 5:5). With the internal temperature of 80 degrees C, the esterification reaction of this solution was carried out at the warm water bath in bottom 2 hours of stirring, and 3, 3', and the solution containing 4 and 4 '- biphenyl tetracarboxylic acid dimethyl ester, 4, 4'-oxy-JIFUTARU acid dimethyl ester (the mole ratio of 3, 3', 4, and 4 '- biphenyl tetracarboxylic acid dimethyl ester, 4, 4'-oxy-JIFUTARU acid dimethyl ester is 5:5) were obtained. After cooling this reaction solution to 50 degrees C, 3 and 4'-oxy-dianyline 142.6g (0.71 mols) was added, the stirring dissolution was carried out for 2 hours, and the uniform polyimide precursor solution was obtained. Furthermore, the polyimide precursor solution (black) was obtained by carrying out the stirring dissolution until it added 2.0g which is 0.5 mass % to the solid content of a polyimide precursor solution which was able to obtain surfactant BYK-302 including a siloxane unit and the system became homogeneity at 25 degrees C (solid content concentration 45 mass %). When the viscosity of this solution was measured, it was 1.5poise at 20 degrees C. Furthermore on the same conditions as an example 1, the spin coat of this solution was similarly carried out to the aluminum substrate (diameter of 100mm) whose SRa is 50nm, heat imide-ization was performed, and the polyimide coat was obtained.

HAJIKI to the substrate of the liquid which carried out coating at the time of coating was not generated. The pinhole was not observed, but the thickness of the obtained polyimide coat is 2 micrometers, and it was [ SRa is 0.5nm and ] very excellent in surface smooth nature.
[0039] Except [ all ] not adding the surfactant which consists of example of comparison 1 silicone oil, it reacted on the same preparation and same conditions as an example 1, and the polyimide precursor solution (black) was obtained (solid content concentration 50 mass %). When the viscosity of this solution was measured, it was 2poise at 20 degrees C. The polyimide coat was made to form furthermore on the aluminum substrate (diameter of 100mm) whose SRa is 50nm on the same approach and same conditions as an example 1 about this solution. Although the thickness of the obtained polyimide coat was 2 micrometers, since there was HAJIKI to the substrate of the liquid which carried out coating at the time of coating, eight pinholes were observed by the polyimide coat. Moreover, SRa was 3nm.
[0040] Except [ all ] making the addition of BYK-302 which are the surfactant of example of comparison 2 example 1 7% (35g) to the solid content of a polyimide precursor solution, it reacted on the same preparation and same conditions as an example 1, and the polyimide precursor solution (black) was obtained (solid content concentration 50 mass %). When the viscosity of this solution was measured, they were 20 degrees C and 1.5poise. The polyimide coat was made to form this solution on a 4 inch-silicon wafer substrate on the same approach and same conditions as an example 1 furthermore. The crack and the crack occurred and the obtained polyimide coat was not able to obtain a uniform coat.
[0041] 3, 3', and 4 and 100g (339.88mmol) of 4'-biphenyl tetracarboxylic dianhydride were dissolved in N-methyl pyrrolidone 392.093g as example of comparison 3 solvent, and it maintained at the room temperature. Subsequently, the solution was gelled, when 3 and 4'-oxy-dianyline 68.04g (339.88mmol) was gradually added over 2 hours in said solution and stirring was continued for further 6 hours. (Solid content concentration 30 mass %)
[0042]
[Effect of the Invention] As mentioned above, even if the polyimide precursor which is a solute contains by the high solid content ratio in a solvent, the polyimide precursor solution of this invention is hypoviscosity, and since it contains the surface active agent including a siloxane unit, HAJIKI to the substrate of the liquid which carried out coating at the time of coating does not occur, and it is not influenced by the condition on the front face of a substrate. Therefore, from this polyimide precursor solution, thickness does not have a pinhole at 10 micrometers or less, and can manufacture the polyimide coat excellent in surface smooth nature with sufficient productivity.

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[Translation done.]

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最終頁に続く

(54)【発明の名称】　ポリイミド前駆体溶液及びそれから得られるポリイミド被膜

(57)【要約】
【課題】　溶媒中に溶質であるポリイミド前駆体が高い固形分比率で含有しても低粘度であり、塗工時塗工液の基板に対するハジキが生ずることがなく、基板表面の状態に影響されにくいポリイミド前駆体溶液、及び膜厚が１０μｍ以下でピンホールがなく、表面平滑性に優れるポリイミド被膜を提供する。
【解決手段】　３，４’－オキシジアニリンと、３，３’，４，４’－ビフェニルテトラカルボン酸及び／又はその誘導体ならびに４，４’－オキシジフタル酸及び／又はその誘導体とからなる塩が溶質として有機溶媒中に溶解しており、これらテトラカルボン酸及び／又はその誘導体のモル比が０：１００～９０：１０であり、溶質としての塩１００質量部に対してシロキサン単位を含む界面活性剤を０．００１～５質量部含有しているポリイミド前駆体溶液。この溶液を基板上に塗工し、イミド化して得られる厚みが１０μｍ以下であるポリイミド被膜。

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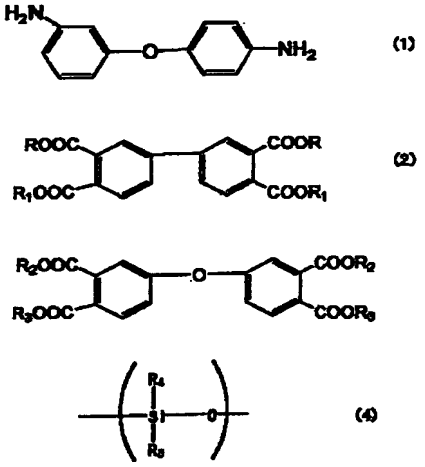
【特許請求の範囲】

【請求項１】　下記式（１）に示す３，４’－オキシジアニリンと、下記式（２）に示す３，３’，４，４’－ビフェニルテトラカルボン酸及び／又はその誘導体ならびに下記式（３）に示す４，４’－オキシジフタル酸及び／又はその誘導体とからなる塩が溶質として有機溶媒中に溶解しており、前記式（２）に示す３，３’，４，４’－ビフェニルテトラカルボン酸及び／又はその誘導体と式（３）に示す４，４’－オキシジフタル酸及び／又はその誘導体とのモル比が０：１００～９０：１０であり、かつ溶質としての塩１００質量部に対して下記式（４）に示すシロキサン単位を含む界面活性剤を０．００１～５質量部含有していることを特徴とするポリイミド前駆体溶液。

【化１】



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（式中Ｒ，Ｒ１，Ｒ２，Ｒ３はそれぞれ独立に水素原子及び炭素数１～５のアルキル基から選ばれ、Ｒ４，Ｒ５はそれぞれ独立に水素原子、炭素数１～５のアルキル基、アルコキシ基及びフェニル基から選ばれる。）

【請求項２】　溶質としての塩の濃度が３０～８０質量％であり、かつ溶液粘度が１０ポイズ以下であることを特徴とする請求項１記載のポリイミド前駆体溶液。

【請求項３】　請求項１又は２に記載のポリイミド前駆体溶液を基板上に塗工し、加熱イミド化して得られる厚みが１０μｍ以下であることを特徴とするポリイミド被膜。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、シロキサン単位を含む界面活性剤を含有するポリイミド前駆体溶液、及びそれから得られるポリイミド被膜に関するものである。

【０００２】

【従来の技術】従来、半導体装置などの各種電子部品の表面保護膜や層間絶縁膜としては電気絶縁性や高耐熱性に優れたポリイミドが広く用いられていた。また、ガラス基板、あるいは透明な有機フィルム上に形成した蛍光

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体に電流を流して発光させる有機エレクトロルミネッセンスディスプレイ（有機ＥＬディスプレイ）では、基板上に陽極、有機ＥＬ層、陰極が順次積層されて構成されるが、前記陽極と前記有機ＥＬ層の間の絶縁膜としてポリイミドの薄膜が使用されている。さらにまた、太陽電池に適用される金属基板上にも絶縁保護膜としてポリイミドが使われている。これら有機ＥＬディスプレイや太陽電池は積層相構造であるので、適用されるポリイミド被膜には、１０μｍ以下の厚みと、優れた表面平滑性ならびにピンホールがないことが要求される。

【０００３】ところでポリイミド被膜を形成させる方法としては、バーコーター法や塗工液を霧状にして基板に吹きつけるスプレーコート法、あるいは遠心力によって塗工するスピンコート法等が知られている。中でもスピンコート法は厚みが１０μｍ以下の薄膜を形成せしめることに好適に用いられている。スピンコート法に用いられる塗工液の粘度は２０℃で１０ポイズ以下にする必要があるが、塗工液の粘度が低いと、塗工時、塗工した液の基板に対するハジキが発生し、被膜にピンホールや表面に微小な凹凸ができたりするという問題があった。

【０００４】一方、ポリイミド被膜を形成する際に用いられるポリイミド塗工液は、ジメチルアセトアミドやＮ－メチルピロリドンを溶媒とし、ポリアミック酸を溶質とするポリイミド前駆体溶液であり、この場合ポリアミック酸の重合度が高く、溶媒への溶解度が小さいことに起因して溶液中の固形分比率を高くすることが困難であった。言いかえるならば、従来のポリアミック酸をポリイミド前駆体としたポリイミド前駆体溶液は、固形分濃度が低いにも関わらず、ポリアミック酸が高重合度であるが故に粘度が高いという本質的な問題があった。このポリアミック酸をポリイミド前駆体としたポリイミド前駆体溶液をスピンコート法によって塗工する場合には、その固形分濃度を極端に低下させる必要があった。従って、従来のポリイミド塗工液から得られるポリイミド薄膜は、塗工液の固形分濃度が低いために、塗工基板表面のわずかなキズや異物、凹凸の跡が被膜表面に残るため、表面平滑性に乏しいという問題があった。

【０００５】以上のように、従来、厚みが１０μｍ以下のポリイミド被膜を得ようとする場合には、ポリイミド塗工液は粘度の低いものを使用しており、粘度の低い塗工液を基板上に塗工すると基板上でのハジキが発生し、また、その結果、得られるポリイミド被膜にピンホールが発生するという問題があった。また、ポリイミド塗工液の固形分濃度が低いと、基板表面の状態に影響されやすく、得られるポリイミド被膜の表面平滑性が低いという問題もあった。

【０００６】

【発明が解決しようとする課題】このような状況に鑑み、本発明の第１の課題は、溶媒中に溶質であるポリイミド前駆体が高い固形分比率で含有しても低粘度であ

り、塗工時に塗工した液の基板に対するハジキが発生せず、基板表面の状態に影響されないポリイミド前駆体溶液を提供すること、また第２の課題は、膜厚が１０μｍ以下でピンホールがなく、表面平滑性に優れるポリイミド被膜を生産性よく提供することにある。

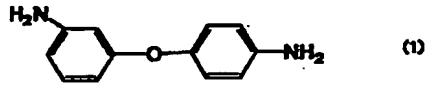
【０００７】

【課題を解決するための手段】本発明者らは、上記の課題を解決するため、鋭意検討を行った結果、有機溶剤に特定のジアミンとカルボン酸及び／又はその誘導体とよりなる塩が溶質として溶解しており、かつ特定の構造単位を有する界面活性剤を含むポリイミド前駆体溶液は、高い固形分比率を有していても低粘度であり、かつ塗工した液の基板に対するハジキがなく、基板表面のキズや凹凸や異物等の基板表面の状態に影響されにくいことを見出した。そして、この溶液から得られるポリイミド被膜は、ピンホールが発生せず、表面平滑性を有していることを見いだし、本発明に到達した。

【０００８】すなわち、本発明の要旨は第１に、下記式（１）に示す３，４’－オキシジアニリンと、下記式（２）に示す３，３’，４，４’－ビフェニルテトラカルボン酸及び／又はその誘導体ならびに下記式（３）に示す４，４’－オキシジフタル酸及び／又はその誘導体とからなる塩が溶質として有機溶媒中に溶解しており、前記式（２）に示す３，３’，４，４’－ビフェニルテトラカルボン酸及び／又はその誘導体と式（３）に示す４，４’－オキシジフタル酸及び／又はその誘導体とのモル比が０：１００～９０：１０であり、かつ溶質としての塩１００質量部に対して下記式（４）に示すシロキサン単位を含む界面活性剤を０．００１～５質量部含有していることを特徴とするポリイミド前駆体溶液である。

【０００９】

【化２】



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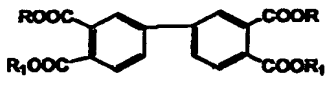

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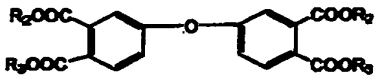
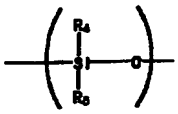


(3)



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【００１０】（式中Ｒ，Ｒ１，Ｒ２，Ｒ３はそれぞれ独立に水素原子及び炭素数１～５のアルキル基から選ばれ、Ｒ４，Ｒ５はそれぞれ独立に水素原子、炭素数１～５のアルキル基、アルコキシ基及びフェニル基から選ばれる。）

第２に前記ポリイミド前駆体溶液において、溶質としての塩の濃度が３０～８０質量％であり、かつ溶液粘度が１０ポイズ以下であることを特徴とするポリイミド前駆体溶液である。第３に前記、ポリイミド前駆体溶液を基板上に塗工し、加熱イミド化して得られる厚みが１０μｍ以下であることを特徴とするポリイミド被膜である。

【００１１】

【発明の実施の形態】以下本発明について詳細に説明する。まず、本発明で用いる用語について説明する。

（１）ポリイミド

ポリマー鎖の繰り返し単位の８０モル％以上がイミド構造を有する有機ポリマーをいう。そして、この有機ポリマーは耐熱性を示す。

（２）ポリイミド前駆体

加熱又は、化学的作用により閉環してポリイミドとなる有機化合物をいう。ここで、閉環とはイミド環構造が形成されることをいう。

（３）ポリイミド前駆体溶液

ポリイミド前駆体が溶媒に溶解しているものである。ここで溶媒とは、２５℃で液状の化合物をいう。

【００１２】（４）粘度

（株）トキメック社製、ＤＶＬ－ＢII型デジタル粘度計（Ｂ型粘度計）を用い、２０℃における回転粘度を測定したものである。

（５）溶質濃度

溶液中に占めるポリイミド前駆体の質量割合を百分率で表した数値である。

（６）ポリイミド被膜の厚み

（株）ミツトヨ製デジマチックマイクロメーターを用い、ポリイミド被膜の厚みを１０箇所で測定し、その平均値として求めたものである。

（７）表面平滑性

３次元表面粗さ測定装置（小阪研究所社製　ＥＴ－３０Ｋ、触針測定）を用い、基板表面又は基板上に形成したポリイミド被膜表面の中心面平均粗さ（ＳＲａ）を測定し、その数値から基板表面又はポリイミド被膜表面の平滑性の評価を行った。

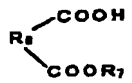
【００１３】さらに、本発明について説明する。本発明のポリイミド前駆体溶液において、溶質である塩は式（１）に示す３，４’－オキシジアニリンと、式（２）に示す３，３’，４，４’－ビフェニルテトラカルボン酸及び／又はその誘導体ならびに式（３）に示す４，４’－オキシジフタル酸及び／又はその誘導体とからなる〔式（２）及び式（３）において、Ｒ，Ｒ１，Ｒ２，Ｒ３はそれぞれ独立に水素原子及び炭素数１～５のアルキル基から選ばる。〕。そして、式（２）に示す３，３’，４，４’－ビフェニルテトラカルボン酸及び／又はその誘導体と式（３）に示す４，４’－オキシジフタ

ル酸及び／又はその誘導体とのモル比は、０：１００～９０：１０が好ましい。式（３）に示す４，４’－オキシジフタル酸及び／又はその誘導体のモル比が１０未満の場合には、得られるポリイミド被膜の基板への密着力が低下して、被膜が基板から剥離する場合がある。

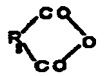
【００１４】本発明のポリイミド前駆体溶液においては、式（２）及び（３）に示すテトラカルボン酸及び／又はその誘導体の一部を、一般式（５）に示すカルボン酸又は一般式（６）に示すジカルボン酸無水物に置き換えてもよい。このとき、式（２）及び（３）に示すテトラカルボン酸及び／又はその誘導体のモル数の和と、一般式（５）に示すカルボン酸又は一般式（６）に示すジカルボン酸無水物とのモル比は１００：０～１００：２０が好ましく、１００：０～１００：１１がさらに好ましい。式（２）及び（３）に示すテトラカルボン酸及び／又はその誘導体モル数の和１００に対する一般式（５）に示すカルボン酸又は一般式（６）に示すジカルボン酸無水物のモル比が２０を超えると強度の低いポリイミド被膜しか得られないことがある。

【００１５】

【化３】



(5)



(6)

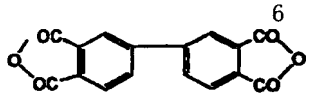
【００１６】〔式中$R_6$は２つのカルボニル基が隣接した炭素原子に直接連結している少なくとも１つの６員環を含む２価の芳香族残基を表し、$R_7$は水素原子又は炭素数１～５のアルキル基を表し、$R_8$は２つのカルボニル基が隣接した炭素原子に直接連結している少なくとも１つの６員環を含む２価の芳香族残基を表す。〕

【００１７】さらに、式（２）及び（３）に示すテトラカルボン酸及び／又はその誘導体の一部を、式（７）に示す３，３’，４，４’－ビフェニルテトラカルボン酸二無水物及び／又は式（８）に示す４，４’－オキシジフタル酸二無水物に置き換えてもよい。このとき、式（２）及び（３）に示すテトラカルボン酸及び／又はその誘導体のモル数の和と、式（７）及び（８）に示すテトラカルボン酸二無水物のモル数の和のモル比は、１００：０～７０：３０が好ましい。このモル比を調節することによってポリイミド前駆体溶液の粘度を微調整することができる。式（７）及び（８）に示すテトラカルボン酸二無水物のモル数の和が３０モル％を超えると本発明の特徴である低粘度なポリイミド前駆体溶液を得ることができないことがある。

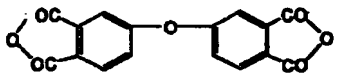
【００１８】

【化４】





(7)



(8)

【００１９】またさらに、式（１）に示す３，４’－オキシジアニリンの一部を、一般式（９）に示す１官能性のアミンに置き換えてもよい。この場合、式（１）に示す３，４’－オキシジアニリンに対する一般式（９）に示すアミンのモル比は１００：０～１００：２０であることが好ましく、１００：０～１００：１１がさらに好ましい。一般式（９）に示すアミンが２０モル％を超えると強度の低いポリイミド被膜しか得られないことがある。〔式中$R_9$は少なくとも１つの６員環を含む芳香族残基を表す。〕

【００２０】

【化５】

(9)

【００２１】また、本発明のポリイミド前駆体溶液には、溶質である塩１００質量部に対して式（４）に示すシロキサン単位を含む界面活性剤〔式中$R_4$，$R_5$はそれぞれ独立に水素原子、炭素数１～５のアルキル基、アルコキシ基及びフェニル基から選ばれる。〕を０．００１～５質量部、好ましくは０．００１～１質量部を含有させる。界面活性剤の含有量が０．００１質量部未満であると、ポリイミド前駆体溶液を基板に塗工した際、塗工した液の基板に対するハジキが発生する場合がある。一方、界面活性剤が５質量部を超えると、製膜性が低下してクラックや割れが発生し、均一な被膜が得られない場合がある。

【００２２】本発明のポリイミド前駆体溶液は、シロキサン単位を含む界面活性剤を前記のような割合で含有させることにより、ガラス基板、セラミック基板、ポリイミド等の有機材基板、アルミ、銅、金、銀、ニッケル等の金属基板に対して塗工した液のハジキが発生しなくなる。

【００２３】本発明で使用できるシロキサン単位を含む界面活性剤としては、入手が容易なレベリング剤、消泡剤、整泡剤等が挙げられ、具体的にはポリエーテル変成したジメチルポリシロキサン、ポリエーテル変成したメチルアルキルポリシロキサン、ポリエステル変成したジメチルポリシロキサン、ポリエステル変成したメチルアルキルポリシロキサン、アラルキル変成したメチルポリシロキサン等が挙げられる。

【００２４】本発明のポリイミド前駆体溶液中のポリイミド前駆体の濃度は、３０～８０質量％であることが好ましい。４０～８０質量％であることがより好ましい。濃度が３０質量％より低いと、塗工する基板表面の傷や異物、凹凸が被膜表面の凹凸として残る場合がある。一

方、濃度が８０質量％より高いと、選定する溶媒の種類によりポリイミド前駆体を安定的に溶解することが困難となる場合があるので好ましくない。

【００２５】本発明のポリイミド前駆体溶液の溶液粘度は、１０ポイズ以下が好ましい。１０ポイズ以上では、塗工液の流動性が十分ではなく、特にスピンコート法において厚みが１０μｍ以下の被膜を作製する場合には、厚みムラが起こりやすく均一な厚みの被膜を作製できない場合があるので好ましくない。

【００２６】本発明におけるポリイミド前駆体溶液は、式（１）に示す３，４’－オキシジアニリンと式（２）に示す３，３’，４，４’－ビフェニルテトラカルボン酸及び／又はその誘導体ならびに式（３）に示す４，４’－オキシジフタル酸及び／又はその誘導体を、有機溶媒に順次添加することにより製造することができる。添加する順序はいかなる順序でもよい。

【００２７】本発明で使用する有機溶媒は、溶質であるポリイミド前駆体と界面活性剤を溶解するものであれば特に限定されないが、たとえばＮ－メチルピロリドン、ジメチルフォルムアミド、ジメチルアセトアミド、ジメチルスルホキシド、ヘキサメチルホスホリルトリアミド、スルホラン、Ｎ，Ｎ’－ジメチルイミダゾリジノン、Ｎ－メチルカプロラクタムなどの分子中にＮ，Ｓ，Ｐ原子を含む極性溶媒やセルソルブ、フェニルセルソルブなどのセルソルブ類、酢酸エチルセルソルブ、酢酸ブチルセルソルブなどの酢酸セルソルブ類、メチルカルビトール、エチルカルビトールなどのカルビトール類、酢酸エチルカルビトール、酢酸ブチルカルビトールなどの酢酸カルビトール類、ジメチルカルビトール（ジグライム）、ジエチルカルビトールなどのカルビトールジエーテル類、シクロヘキサノール、ベンジルアルコールなどのアルコール類、シクロヘキサノン、イソホロンなどのケトン類、γ－ブチロラクトンなどが挙げられる。

【００２８】本発明のポリイミド前駆体溶液からポリイミド被膜を得るための塗工方法としては通常の方法が採用され、例えば、スピンコート法、スプレイコート法及びバーコーター法等の方法が挙げられ、厚みが１０μｍ以下の表面平滑性に優れた薄膜を作製する場合には、スピンコート法が好適に用いられる。スピンコート法以外の塗工方法においても、本発明のポリイミド前駆体溶液を用いると、従来のポリイミド前駆体溶液を用いてポリイミド被膜を製造する場合に比較して、表面平滑性に優れたポリイミド被膜を得ることができる。

【００２９】ポリイミド被膜は、ポリイミド前駆体溶液を基板もしくは基材上に塗工し、乾燥して溶媒を除去した後、ポリイミド前駆体の塗膜を得、これをイミド化してポリイミド被膜を得る。さらに、基材から剥離して、あるいはポリイミド前駆体の塗膜を基材から剥離してイミド化するとポリイミドフィルムが得られる。本発明においてポリイミドフィルムはポリイミド被膜の範疇に入るものである。イミド化は１５０℃以上、好ましくは２００℃以上、より好ましくは２５０℃以上で、１０分間以上、好ましくは３０分間以上加熱して行う。

【００３０】さらに、本発明のポリイミド前駆体溶液には、必要に応じて例えば、顔料、導電性のカーボンブラック及び金属粒子のような充填剤、摩滅剤、誘電体、潤滑剤等の他公知の添加物を本発明の効果を損なわない範囲で添加することができる。また、他の重合体や例えば水不溶性のエーテル類、アルコール類、ケトン類、エステル、ハロゲン化炭化水素類、炭化水素類等の溶媒を本発明の効果を損なわない範囲で添加することができる。

【００３１】本発明のポリイミド前駆体溶液から得られるポリイミド被膜、特に１０μｍ以下の厚みのポリイミド被膜においては、ピンホールを含まず、かつ基板表面のキズや異物や凹凸に関係無く優れた表面平滑性を有するので、表面保護膜、層間絶縁膜等として好適に用いられ、例えば、太陽電池基板、ＥＬ素子基板、耐熱絶縁用素子、コンデンサー等に用いられる。また、本発明のポリイミド前駆体溶液においても、これらの製品の製造に用いることができる。

【００３２】

【実施例】以下、本発明を実施例を用いて詳細に説明する。

実施例１

溶媒としてのＮ－メチルピロリドン５００ｇに４，４’－オキシジフタル酸（ＯＤＰＡ）２７０．０ｇ（０．８７ｍｏｌ）を溶解し、次いでメタノール８３．５６ｇ（２．６１ｍｏｌ）とトリエチルアミン４．１８ｇを添加した。この溶液を温水浴にて内温８０℃で、撹拌下２時間にてエステル化反応させ、４，４’－オキシジフタル酸ジメチルエステルを含有する溶液を得た。この反応溶液を５０℃まで冷却した後、３，４’－オキシジアニリン１７４．２９ｇ（０．８７ｍｏｌ）を添加し、２時間撹拌溶解し、均一なポリイミド前駆体溶液を得た。さらに、シロキサン単位を含む界面活性剤ＢＹＫ－３０２（ビッグケミー・ジャパン（株）社製、ポリエーテル変成したジメチルポリシロキサン）を、得られたポリイミド前駆体溶液の固形分に対して０．５質量％である２．５ｇを添加し、２５℃にて系が均一になるまで撹拌溶解して、ポリイミド前駆体溶液（黒色）を得た（固形分濃度５０質量％）。この溶液の粘度を測定したところ、２０℃で１．８ポイズであった。さらにこの溶液をスピンコーター（ミカサ（株）社製、１Ｈ－ＤＸ）を用いて回転数４，０００ｒｐｍ、３０秒にて８インチーシリコンウエハー基板上に塗工した。この際、塗工した液の基板に対するハジキは発生しなかった。その後、塗工した液を窒素雰囲気下８０℃で５時間乾燥した後、窒素雰囲気下３００℃で５時間加熱イミド化を行い、厚み２μｍのポリイミド被膜を得た。このポリイミド被膜内のピンホールは観察されなかった。

【００３３】さらに、同溶液を、中心面平均粗さ（ＳＲａ）が５０ｎｍであるアルミ基板（直径１００ｍｍ）に、同様にスピンコートし、熱イミド化を行ない、ポリイミド被膜を得た。得られたポリイミド被膜は、厚みが２μｍで、ピンホールは観察されず、さらにＳＲａは０．５ｎｍであり、非常に表面平滑性に優れたものであった。

【００３４】実施例２

塗工基板として、中心面平均粗さ（ＳＲａ）が４０ｎｍであり、直径１００ｍｍのガラス基板を用いた以外は全て実施例１と同様な方法でポリイミド被膜を形成させた。塗工時には、塗工した液の基板に対するハジキは発生しなかった。得られたポリイミド被膜は、膜厚が２μｍであり、ピンホールは観察されず、ＳＲａが０．７ｎｍであり、表面平滑性に優れるものであった。

【００３５】実施例３

界面活性剤を、シロキサン単位を含むＢＹＫ－３３３（ビッグケミー・ジャパン（株）社製、ポリエーテル変成したジメチルポリシロキサン）にする以外は全て実施例１と同様の仕込みと条件で反応を行い、ポリイミド前駆体溶液（黒色）を得た。この溶液の粘度を測定したところ、２０℃、１．８ポイズであった。さらにこの溶液を実施例１と同様な方法ならびに条件で、ＳＲａが５０ｎｍであるアルミ基板（直径１００ｍｍ）上にポリイミド被膜を形成させた。塗工時には、塗工した液の基板に対するハジキは発生しなかった。得られたポリイミド被膜の厚みは２μｍで、被膜面内のピンホールは観察されず、かつＳＲａは０．４ｎｍであった。

【００３６】実施例４

界面活性剤を、シロキサン単位を含むＳＨ１９３（東レダウコーニング社製、変成シリコーンオイル）にする以外は全て実施例１と同様の仕込みと条件で反応を行い、本発明のポリイミド前駆体溶液（黒色）を得た。この溶液の粘度は、２０℃で１．８ポイズであった。さらにこの溶液を実施例１と同様な方法ならびに条件で、ＳＲａが５０ｎｍであるアルミ基板（直径１００ｍｍ）上にポリイミド被膜を形成させた。塗工時には、塗工した液の基板に対するハジキは発生しなかった。得られたポリイミド被膜の厚みは２μｍで、被膜面内のピンホールは観察されず、かつＳＲａは０．５ｎｍであった。

【００３７】実施例５

溶媒としてのＮ－メチルピロリドン５００ｇに３，３’，４，４’－ビフェニルテトラカルボン酸（ＢＰＤＡ）７０．９ｇ（０．２４ｍｏｌ）ならびに４，４’－オキシジフタル酸（ＯＤＰＡ）１７４．５ｇ（０．５６ｍｏｌ）を溶解し、次いでメタノール７７．１３ｇ（０．２４ｍｏｌ）とトリエチルアミン３．８６ｇを添加した（ＢＰＤＡとＯＤＰＡのモル比は７：３）。この溶液を温水浴にて内温８０℃で、撹拌下２時間にてエステル化反応させ、３，３’，４，４’－ビフェニルテトラカルボン酸ジメチルエステルと４，４’－オキシジフタル酸ジメチルエステル（３，３’，４，４’－ビフェニルテトラカルボン酸ジメチルエステルと４，４’－オキシジフタル酸ジメチルエステルのモル比は７：３）を含有する溶液を得た。この反応溶液を５０℃まで冷却した後、３，４’－オキシジアニリン１６０．９ｇ（０．８０ｍｏｌ）を添加し、２時間撹拌溶解し、均一なポリイミド前駆体溶液を得た。さらに、シロキサン単位を含む界面活性剤ＢＹＫ－３０２（ビッグケミー・ジャパン（株）社製、ポリエーテル変成したジメチルポリシロキサン）を、得られたポリイミド前駆体溶液の固形分に対して０．５質量％である２．３ｇを添加し、２５℃にて系が均一になるまで撹拌溶解することにより、ポリイミド前駆体溶液（黒色）を得た（固形分濃度４８質量％）。この溶液の粘度を測定したところ、２０℃で１．７ポイズであった。さらにこの溶液を実施例１と同様な条件で、スピンコーターを用いて８インチーシリコンウエハー基板上に塗工した。この際、塗工した液の基板に対するハジキは発生しなかった。その後、塗工物を窒素雰囲気下８０℃で５時間乾燥した後、窒素雰囲気下３００℃で５時間加熱イミド化を行い、厚み２μｍのポリイミド被膜を得た。このポリイミド被膜にはピンホールは観察されなかった。さらに、同溶液を、ＳＲａが５０ｎｍであるアルミ基板（直径１００ｍｍ）に、同様にスピンコートし、熱イミド化を行ない、ポリイミド被膜を得た。得られたポリイミド被膜は、厚みが２μｍで、ピンホールは観察されず、さらにＳＲａは０．５ｎｍであり、非常に表面平滑性に優れたものであった。

【００３８】実施例６

溶媒としてのＮ－メチルピロリドン５００ｇに３，３’，４，４’－ビフェニルテトラカルボン酸（ＢＰＤＡ）１０４．８ｇ（０．３６ｍｏｌ）ならびに４，４’－オキシジフタル酸（ＯＤＰＡ）１１０．５ｇ（０．３６ｍｏｌ）を溶解し、次いでメタノール６８．３７ｇ（２．１３ｍｏｌ）とトリエチルアミン３．４２ｇを添加した（ＢＰＤＡとＯＤＰＡのモル比は５：５）。この溶液を温水浴にて内温８０℃で、撹拌下２時間にてエステル化反応させ、３，３’，４，４’－ビフェニルテトラカルボン酸ジメチルエステルと４，４’－オキシジフタル酸ジメチルエステル（３，３’，４，４’－ビフェニルテトラカルボン酸ジメチルエステルと４，４’－オキシジフタル酸ジメチルエステルのモル比は５：５）を含有する溶液を得た。この反応溶液を５０℃まで冷却した後、３，４’－オキシジアニリン１４２．６ｇ（０．７１ｍｏｌ）を添加し、２時間撹拌溶解し、均一なポリイミド前駆体溶液を得た。さらに、シロキサン単位を含む界面活性剤ＢＹＫ－３０２を、得られたポリイミド前駆体溶液の固形分に対して０．５質量％である２．０ｇを添加し、２５℃にて系が均一になるまで撹拌溶解することにより、ポリイミド前駆体溶液（黒色）を得た（固

形分濃度４５質量%）。この溶液の粘度を測定したところ、２０℃で１．５ポイズであった。さらにこの溶液を実施例１と同様な条件で、ＳＲａが５０ｎｍであるアルミ基板（直径１００ｍｍ）に、同様にスピンコートし、熱イミド化を行ない、ポリイミド被膜を得た。塗工時に塗工した液の基板に対するハジキは発生しなかった。得られたポリイミド被膜は、厚みが２μｍで、ピンホールは観察されず、ＳＲａは０．５ｎｍであり、非常に表面平滑性に優れたものであった。

【００３９】比較例１

シリコーンオイルからなる界面活性剤を添加しない以外は全て実施例１と同様の仕込みと条件で反応を行い、ポリイミド前駆体溶液（黒色）を得た（固形分濃度５０質量%）。この溶液の粘度を測定したところ、２０℃で２ポイズであった。さらにこの溶液を実施例１と同様な方法ならびに条件でＳＲａが５０ｎｍであるアルミ基板（直径１００ｍｍ）上にポリイミド被膜を形成させた。得られたポリイミド被膜の厚みは２μｍであったが、塗工時に塗工した液の基板に対するハジキがあったために、ポリイミド被膜にはピンホールが８個観察された。また、ＳＲａは３ｎｍであった。

【００４０】比較例２

実施例１の界面活性剤であるＢＹＫ－３０２の添加量を、ポリイミド前駆体溶液の固形分に対して７%（３５ｇ）にする以外は全て実施例１と同様の仕込みと条件で＊反応を行い、ポリイミド前駆体溶液（黒色）を得た（固形分濃度５０質量%）。この溶液の粘度を測定したところ、２０℃、１．５ポイズであった。さらにこの溶液を実施例１と同様な方法ならびに条件で４インチーシリコンウエハ基板上にポリイミド被膜を形成させた。得られたポリイミド被膜はクラックや割れが発生し、均一な被膜を得ることができなかった。

【００４１】比較例３

溶媒としてのＮ－メチルピロリドン３９２．０９３ｇに３，３’，４，４’－ビフェニルテトラカルボン酸二無水物１００ｇ（３３９．８８ｍｍｏｌ）を溶解し、室温に保った。次いで前記溶液に３，４’－オキシジアニリン６８．０４ｇ（３３９．８８ｍｍｏｌ）を２時間にわたり徐々に添加し、さらに６時間撹拌を続けたところ、溶液はゲル化した。（固形分濃度３０質量%）

【００４２】

【発明の効果】以上のように、本発明のポリイミド前駆体溶液は、溶媒中に溶質であるポリイミド前駆体が高い固形分比率で含有しても低粘度であり、かつシロキサン単位を含む界面活性剤を含んでいるので、塗工時に塗工した液の基板に対するハジキが発生せず、基板表面の状態に影響されない。したがって、このポリイミド前駆体溶液からは、膜厚が１０μｍ以下でピンホールがなく、表面平滑性に優れたポリイミド被膜を生産性よく製造することができる。

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フロントページの続き

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